Journal of Power Sources 240 (2013) 241–244

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Short communication

Enhancing the performance of doped ceria interlayer for tubular solid oxide fuel cells

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HIGHLIGHTS

- Impregnation is first proposed to enhance the doped ceria interlayer performance.
- The interlayer resistance is substantially reduced with ion impregnation.
- Peak power density of tubular cells increases from 1.01 to 1.50 W cm^{-2} at 750 °C.

ARTICLE INFO

Article history:
Received 11 March 2013
Received in revised form
2 April 2013
Accepted 3 April 2013
Available online 10 April 2013

Keywords:
Tubular solid oxide fuel cells
Bi-layer electrolyte
Doped ceria interlayer
Impregnation
Yttria-stabilized zirconia

ABSTRACT

Doped ceria interlayer fabricated by conventional wet ceramic process such as dip-coating often suffers from high resistance due to either low density or solid-state reaction with yttria-stabilized zirconia (YSZ) electrolyte in solid oxide fuel cells (SOFCs). This work presents a new route to reduce the resistance by increasing the density while minimizing the solid-state reaction through impregnating samaria-doped ceria (SDC) nano-particles to porous SDC interlayer of anode-supported tubular SOFCs. Results show that impregnated fine structure can substantially reduce the ohmic resistance, from 0.140 to 0.087 Ω cm^2 at 750 °C, and consequently significantly improve the fuel cell performance, peak power density from 1.01 to 1.50 W cm^{-2} at 750 °C. The significant improvements demonstrate that impregnation is an effective method to improve the interlayer performance.

1. Introduction

As high efficiency energy conversion devices, solid oxide fuel cells (SOFCs) have been intensively studied to accelerate its commercialization step [1]. One approach is to low its operating temperature by using thin-film electrolyte of yttria-stabilized zirconia (YSZ) and developing novel cathode materials, such as cobalt-containing perovskite oxides, which are highly catalytic for oxygen reduction. Among these materials, composites consisting of $Sm_{0.5}Sr_{0.5}CoO_3$ (SSC) and $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) have shown great promise as cathodes for intermediate and low temperature SOFCs [2]. However, YSZ reacts with SSC as well as other strontium doped perovskites containing cobalt. The reaction forms insulating phase of $SrZrO_3$ at the cell fabrication temperatures [3]. Therefore, a doped ceria (DCO) interlayer is proposed as a protective layer to avoid possible reaction between YSZ and SSC. Accordingly, various fabrication techniques are developed to manufacture the interlayer. Wet ceramic processes like screen-printing and dip-coating are widely applied to fabricate the interlayer since these techniques are readily available, cost effective, and applicable to various cell designs [4,5]. However, such application in fabricating DCO interlayer is impeded by the sintering step, difficult to obtain a dense interlayer with low resistance. At high temperatures such as 1500 °C, the interlayer can be densified in the case of co-sintering the anode-supported YSZ electrolyte/DCO interlayer due to the sinterability of the DCO interlayer and the shrinkage of the support [6]. However, severe solid-state reaction occurs between YSZ and doped ceria at high temperature [7], which results in increased ohmic resistance and thus reduces the power density. For example, $Gd_{0.2}Ce_{0.8}O_{1.9}$ (GDC) reacts readily with YSZ at 1500 °C to form ZrO_2–CeO_2–Y_2O_3–Gd_2O_3 solid solutions. The conductivity for $(GDC)_{0.5}(YSZ)_{0.5}$ at 700 °C is only 0.001 S cm^{-1},

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http://dx.doi.org/10.1016/j.jpowsour.2013.04.007

much lower than that for either YSZ (0.023 S cm^{-1}) or GDC (0.038 S cm^{-1}) [8]. As for preparing the interlayer on the sintered anode-supported YSZ electrolyte, it is difficult to obtain a dense interlayer even at high sintering temperature, in addition to the adverse solid-state reaction. At low temperature, the solid-state reaction could be minimized but the interlayer could not be densified at all, which also results in high ohmic resistance. The optimum temperature is reported to be 1200 °C, at which the interlayer is still very porous while the solid-state reaction is negligible [4,9]. Physical deposition processes which can fabricate dense oxides at relatively low temperature are therefore used to fabricate dense interlayer without the formation of an insulting interface, including pulsed laser deposition, aerosol deposition, and plasma-beam sputtering deposition [9–11]. However, the development of these techniques is limited by the high requirement for equipments and complex process control, and thus leading to the vast production cost. In addition, it is difficult to produce uniform interlayer for cells with non-planar structure such as tubular SOFCs.

In this work, a fabrication process is proposed to increase the density of the SDC interlayer which is fabricated by wet ceramic techniques, and consequently decrease the ohmic resistance and improve the cell performance. The density is increased by impregnation technique, which is usually applied to fabricate nano-structure electrodes for SOFCs [12]. The new process is successfully demonstrated with tubular SOFCs, which have many advantages such as ease in sealing and the ability to endure the thermal stress caused by rapid heating and cooling [13,14].

2. Experimental

Fig. 1 outlines the new fabrication route, where impregnation is conducted after the interlayer is slurry coated and fired at 1200 °C so as to minimize the solid-state reaction between SDC–YSZ [4,9]. The tubular NiO–YSZ substrate with thin YSZ electrolyte was fabricated using a simple dip-coating and co-sintering method. The details of fabrication process have been represented by Liu et al. [15]. The tube is approx. 1.7 cm long, 1.0 cm in outside diameter, and 0.4 mm thick. Unless otherwise specified, all the starting chemicals were from Sinopharm Chemical Reagent Co. Ltd. The anode support consists of 50 wt.% NiO (Lanzhou Jinchuan Metal Material Technology Co., China) and 50 wt.% YSZ (Farmeiya Advanced Materials Co., China). Fine YSZ (TOSOH Co.) powder was used to fabricate the thin electrolyte layer by dip-coating.

SDC interlayer was prepared via dip-coating, a typical wet ceramic process. SDC powders were prepared using the glycine–nitrate method with $Sm(NO_3)_3$ and $(NH_4)_2Ce(NO_3)_6$ as the precursors [16]. The dip-coating process was performed by dipping the tubular substrate into the SDC suspension and subsequently drying in air. The coated SDC was then fired at 1200 °C for 2 h, resulting in a porous SDC interlayer, which is consistent with the literatures [4,9].

The impregnation cycle was conducted by dipping the tube into a 1 mol L^{-1} SDC solution containing glycine, $Sm(NO_3)_3$ and $(NH_4)_2Ce(NO_3)_6$, drawing up, drying, and firing at 800 °C for 2 h. The SDC loading was determined by weighting the sample before and after the cycle. The SDC mass increased about 40% after the ninth cycle. Finally, the SDC interlayer was fired at 1200 °C for 2 h to enhance the connection of SDC particles.

SSC–SDC cathode was fabricated by brush-printing technique. SSC–SDC slurry was prepared by mechanically mixing SSC and SDC powders (at a weight ratio of 7:3) with organic additives such as terpilenol and ground with agate mortar. SSC–SDC slurry was then painted to SDC interlayer and fired at 950 °C for 2 h. The cathode active area is 0.6 cm^2. For comparison purpose, the cell with SDC interlayer, which was fired at 1200 °C twice without conducting the impregnation cycle, was also fabricated.

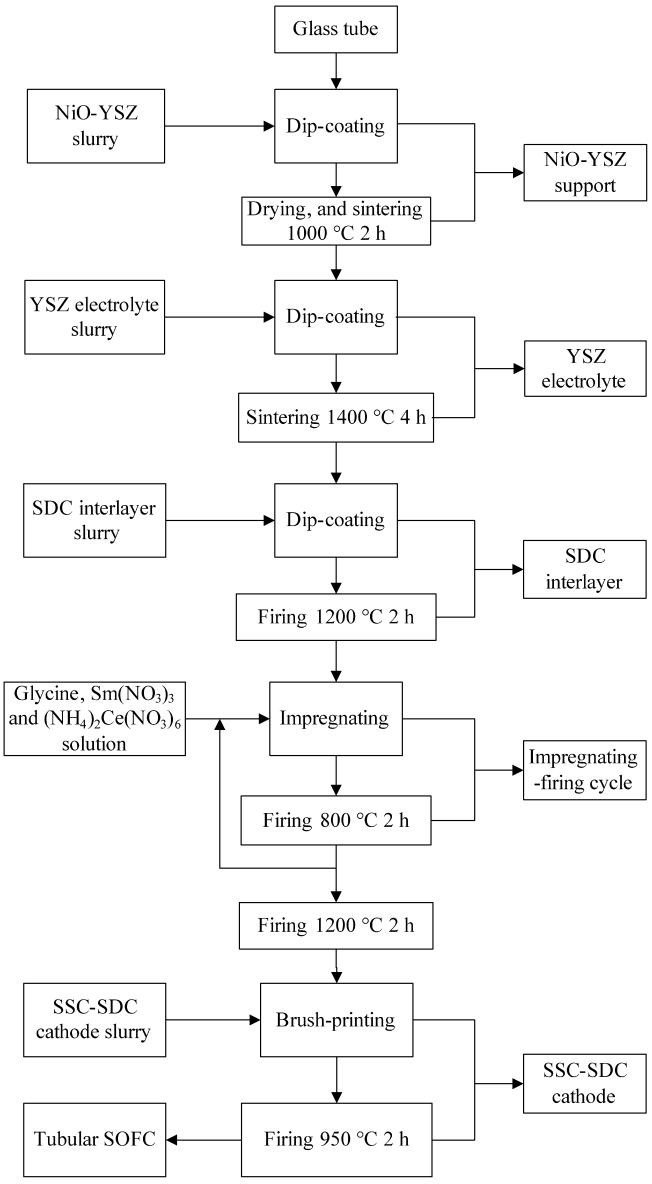

Fig. 1. Fabrication route for the tubular cell with bi-layer YSZ/SDC electrolyte where the interlayer is enhanced with impregnation.

The tubular cell was sealed to quartz tube with silver paste (DAD-87, Shanghai Synthetic Resin Institute). A four-probe setup was used to eliminate the resistive losses in the Ag current-collecting wires. Electrochemical performance measurements were conducted at temperature range of 600–750 °C using a Zahner Zennium electrochemical station. Air was used as oxidant and humidified hydrogen flow was controlled at 70 ml min^{-1} in the anode side. The impedance spectra were recorded under open circuit conditions with amplitude of 10 mV over the frequency range, 1 MHz–0.1 Hz. The microstructure was characterized by scanning electron microscopy (SEM, JSM-6700F).

3. Results and discussion

Fig. 2a shows the cross-sectional micrograph of the four-layered structure. The thicknesses of the YSZ electrolyte, SDC interlayer,

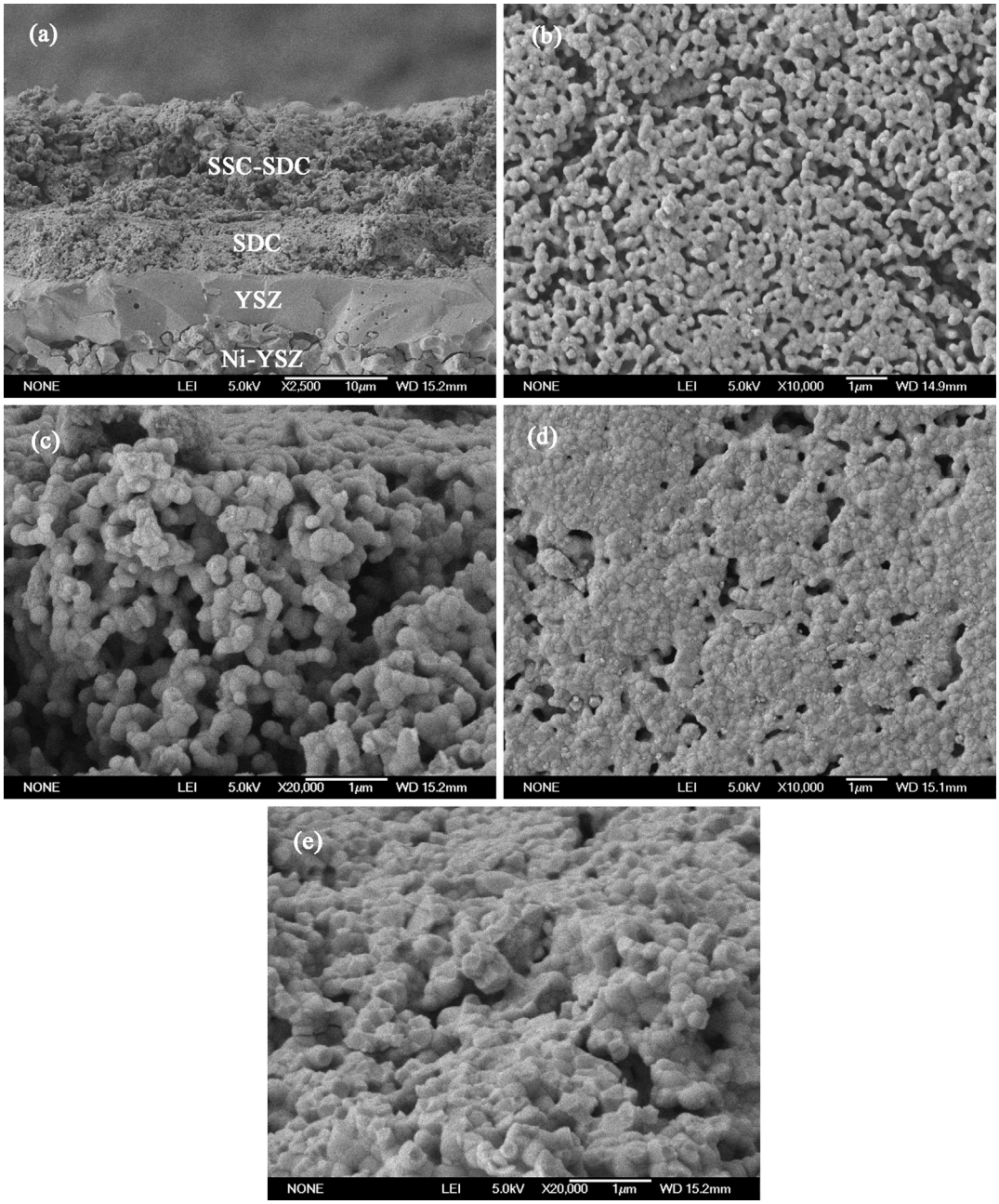

Fig. 2. SEM images of (a) cross-sectional view of the four-layer cell; (b) surface and (c) cross-sectional view of the SDC interlay; (d) surface and (e) cross-sectional view of the SDC interlay after impregnation treatment.

SSC–SDC cathode are about 6.6, 6.2, and 12.3 μm, respectively. The YSZ layer is very dense with a few isolated pores while the Ni–YSZ anode and SSC–SDC cathode are porous. Fig. 2b and c presents the microstructures of the SDC interlayer without conducting the impregnation process. The slurry-coated layer is very porous due to the relatively low firing temperature (1200 °C) to avoid the possible solid-state reaction between SDC and YSZ. The porous character is consistent with that reported in the literatures [4,9]. The porosity of the interlayer is about 45% as estimated with its weight, diameter, length, and thickness. After impregnation treatment, the interlayer becomes much denser although pores still can be seen on the SEM pictures as shown in Fig. 2d and e. The porosity decreases to 42% for the first impregnation cycle. However, the impregnating treatment becomes less efficient after each cycle. The porosity is estimated to be 22% for the sample shown in Fig. 2d and e, which is prepared with 9 cycles.

Increasing the density eventually reduces the bi-layer electrolyte resistance, which is approximately the ohmic resistance determined with electrochemical impedance for a single cell since the ohmic contribution from the electrodes is often negligible, while the polarization resistance is not affected for the SSC–SDC composite cathode and the Ni–YSZ anode. The resistance for YSZ/SDC bi-layer electrolyte without impregnation treatment is 0.172 Ω cm^2 at 750 °C. It decreases to 0.119 Ω cm^2 when the impregnation cycle has been repeated 9 times. If YSZ resistance is deducted according to its conductivity and thickness [17], it is

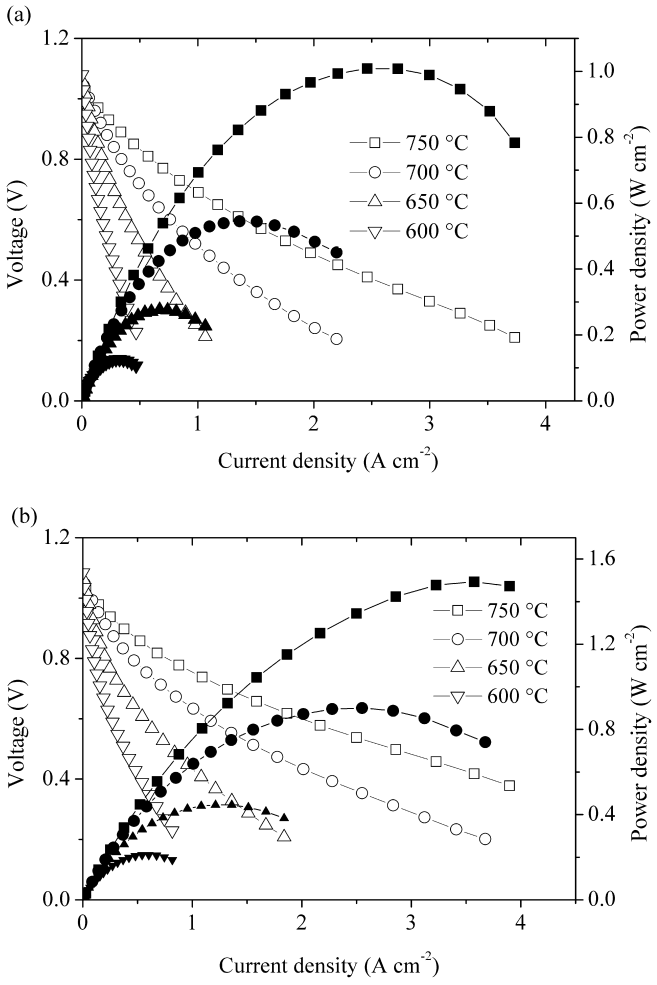

Fig. 3. P–V–I curves for the cells (a) without, and (b) with SDC impregnation treatment.

0.140 Ω cm^2 for the slurry-coated SDC interlayer and 0.087 Ω cm^2 for the interlayer with impregnated SDC. Although the resistance is still higher than that predicted from a fully dense interlayer, which is 0.013 Ω cm^2 at 750 °C for 6.2 μm thick dense SDC electrolytes [18], the reduction in ohmic resistance is significant, about 38%. The significant reduction probably results from the increased density of the SDC interlayer thus enhanced electrical conductivity, and expanded contact area between the SDC interlayer and YSZ electrolyte.

Reducing the electrolyte resistance should improve the cell performance when the polarization resistance remains unchanged. Fig. 3a shows the P–V–I curves for the cell without impregnation. Open circuit voltages (OCVs) are close to the theoretical values, which indicates dense YSZ electrolyte, in agreement to the SEM observation, Fig. 2a. The peak power densities are 1.01, 0.54, 0.27, 0.13 W cm^{-2} at 750, 700, 650, and 600 °C, respectively. The performance is superior to those reported for tubular SOFCs based on YSZ electrolytes without interlayers [15,19]. And it is comparable to those reported for planar cells using bi-layer YSZ/SDC electrolytes [5,20]. After the interlayer is treated with the impregnation process, the performance is greatly improved, Fig. 3b. At 750 °C, the peak power density increases to 1.50 W cm^{-2}. The performance is comparable to a planar cell with doped ceria interlayer prepared by the sputtering technique [11]. In comparison, our method has the advantages of simple operation, no special requirement for devices, and application to complicated cell design.

4. Conclusion

The performance of the SDC interlayer fabricated with ceramic coating technique is greatly enhanced with fine structures using the impregnation method. A porous SDC interlayer is dip-coated on thin YSZ electrolyte for tubular SOFC and subsequently firing at only 1200 °C to minimize the solid-state reaction between SDC and YSZ. After the impregnating-firing cycles, the porosity of the SDC interlayer is reduced and the connection of SDC particles is enhanced, resulting in an obvious decrease in the ohmic resistance and thus significant increase in the cell output. For example, the ohmic resistance for the SDC interlayer decreases from 0.140 to 0.087 Ω cm^2, and the peak power density of the cell increases from 1.01 to 1.50 W cm^{-2} at 750 °C. While significant effort is now focused on finding new materials and developing highly skilled processes, our results demonstrate a feasible approach for fabricating SDC interlayer with high performance.

Acknowledgments

We thank gratefully the financial support of the Ministry of Science and Technology of China (2012CB215403). Shuang Wang is also grateful to National Nature Science Foundation of China (J1030412).

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